

(19) Japan Patent Agency (JP)

(12) Public Patent bulletin (A)

(11) Public Patent Application Number

Tokkai 2002 - 97217

(P2002 - 97217A)

(43) Date of being Public

Heisei 14, 2<sup>nd</sup> March (2002. 4. 2)

(51) Int. Cl.<sup>7</sup>

Discrimination

Number

C 08 F 2/48

2/38

20/38

290/06

299/02

FI

Theme code (reference)

C 08 F 2/48

4J011

2/38

4J027

20/38

4J038

290/06

4J040

299/02

4J100

Investigation of Claims Nil

Number of Inventions 9

OL (Total 14 Pages (Japanese))

Continued on the last page

(21) Patent Application Number

Tokkai 2000 - 292459 (P2000 - 292459)

(22) Date of Patent Application

Heisei 12 26<sup>th</sup> September (2000. 9. 26)

(71) Patent Applicant

000005968

Mitsubishi Kagaku Kabushiki Kaisha  
(Mitsubishi Chemicals Co. Ltd.)

Tokyo to, Chiyoda ku, Marunouchi, 2  
cho me, 5 ban, 2 go.

(72) Inventor

Chokai Takashi

Ibaraki ken, Inashiki gun, Ami cho,

P2002 - 97217

Page

Chuo, 8 cho me, 3 ban, 1 go.  
Mitsubishi Kagaku Kabushiki Kaisha  
Tsukuba Kenkyusho Nai  
(Internal to Tsukuba Research Center  
of Mitsubishi Chemicals Co. Ltd.)  
Miki Yasuaki  
Ibaraki ken, Inashiki gun, Ami cho,  
Chuo, 8 cho me, 3 ban, 1 go.  
Mitsubishi Kagaku Kabushiki Kaisha  
Tsukuba Kenkyusho Nai  
(Internal to Tsukuba Research Center  
of Mitsubishi Chemicals Co. Ltd.)

(72) Inventor

(74) Representative  
Patent Attorney

100103997

Hasegawa Shoji

Continued on the last page

(54) [Title of the invention]

Photo-Hardening Composite and Its Hardened Material.

(57) [Summary]

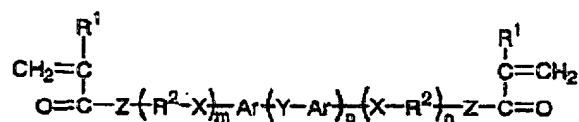
[Topic]

To offer a composite that has excellent storage stability, shows satisfactory hardening property by active energy ray irradiation such as ultraviolet rays, has excellent handling property and excellent balance between refractive index and flowability, and optical material having high refractive index and transparency after hardening.

[Method for solution]

The photo-hardening composite that has the characteristic of containing sulfur-containing (metha) acrylate compound shown by the general formula (I) or radical reactive composite containing the same (A), 0.001 ~ 0.5 parts by weight of polymerization preventing agent (B) with respect to 100 parts by weight of component (A) and polymerization initiator (C).

[Formula 1]



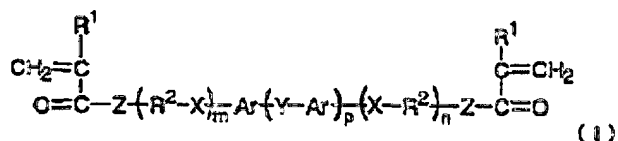
[Scope of patent claims]

[Claim 1]

The photo-hardening composite has the characteristic of containing sulfur-containing

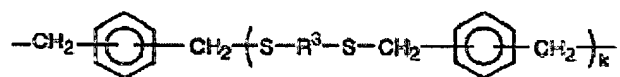
(metha) acrylate compound shown by the general formula (I) or radical reactive composite containing the same (A), 0.001 ~ 0.5 parts by weight of polymerization preventing agent (B) with respect to 100 parts by weight of component (A) and polymerization initiator (C).

[Formula 1]



[Wherein, R<sup>1</sup> shows hydrogen atom or methyl radical, R<sup>2</sup> shows univalent hydrocarbon radical having 1 ~ 12 carbon atoms, Ar shows arylene radical having 6 ~ 30 carbon atoms that can be substituted with halogen atom excluding fluorine atom or alalkylene having 7 ~ 30 carbon atoms that can be substituted with halogen atom excluding fluorine atom, X shows - O - or - S -, when X shows - O -, Y shows - S - or - SO<sub>2</sub> - and when X shows - S -, Y shows - S -, - SO<sub>2</sub> -, - CO -, alkylene radical having 1 ~ 12 carbon atoms, alalkylene radical having 7 ~ 30 carbon atoms, - Ar - (Y - Ar)<sub>p</sub> - shows radical chosen from oligomer shown by

[Formula 2]



(Wherein, R<sup>3</sup> shows alkylene radical having 1 ~ 12 carbon atoms that can possess ether bond, k shows average oligomerization degree and is 1 ~ 5) or oligomer shown by

[Formula 3]



(Wherein, l shows average oligomerization degree and is 1 ~ 5), Z shows - O - or - S -, m and n are integers from 1 ~ 5 and p is integer from 0 ~ 10.]

[Claim 2]

The photo-hardening composite described above in claim number 1 in which the component (C) is used with the quantity of 0.01 ~ 10 parts by weight with respect to 100 parts by weight of component (A).

[Claim 3]

The photo-hardening composite described above in claim number 1 or 2 in which weight ratio of component (C) and (B) ((C) / (B)) is within the range from 0.05 ~ 5000.

[Claim 4]

The photo-hardening composite described above in claim numbers 1 ~ 3 in which the polymerization initiator contains phosphorus.

[Claim 5]

The hardened material formed by hardening the photo-hardening composite described above in any one of the claim numbers from 1 ~ 4.

[Claim 6]

The resin composite used for optical lens that is formed by containing photo-hardening composite described above in any one of the claim numbers from 1 ~ 4.

[Claim 7]

The resin composite used for optical parts that is formed by containing photo-hardening composite described above in any one of the claim numbers from 1 ~ 4.

[Claim 8]

The resin composite used for reflection preventing coating that is formed by containing photo-hardening composite described above in any one of the claim numbers from 1 ~ 4.

[Claim 9]

The resin composite used for adhesive that is formed by containing photo-hardening composite described above in any one of the claim numbers from 1 ~ 4.

[Detailed description of the invention]

[0001]

[Industrial applicability]

The present invention relates to photo-hardening composite that has excellent storage stability and that shows satisfactory hardening property by active energy rays irradiation such as ultraviolet rays. This composite is suitable to be used in the manufacture of optical lens having high refractive index and transparency, optical part, reflection preventing coating, adhesive etc.

[0002]

[Techniques of the past]

As regards the multifunctional (metha) acrylate having high refractive index, acrylate possessing fluorene ring as described in Patent number Hei 4 – 337307, Hei 5 – 164903, Hei 6 – 220131, Hei 10 – 67970, Hei 10 – 67977, sulfur-containing (metha) acrylate such as bis (4 – methacryloyl thio phenyl) sulfide as described in Patent number Hei 2 – 160762, Hei 5 – 142501, Hei 6 – 3628, halogen-containing (metha) acrylate such as 2, 2' – bis (3, 5 – di bromo – 4 – (2 – methacryloyloxy ethoxy) phenyl) propane etc. as described in Patent number Sho 58 – 52601, Hei 1 – 135853, Hei 3 – 36582 are being used since past, however, these are solid having melting point of more than 150<sup>0</sup>C. When molecules of these (metha) acrylates is designed such that refractive index becomes high, then introduction of atom groups such as halogen atom such as bromine, iodine etc., benzene ring, sulfur are required as a result it can be made liquid at normal temperature.

[0003]

Moreover, when these atom groups are introduced, flowability is required at the time of

injection molding or coating due to which large quantity of diluting monomer is required as a result refractive index drops. Therefore, in the case of using it as main component, its handling property, storage stability (particularly, stability at the time of heating) become bad as it has to be injection molded by heating up to the temperature exceeding 60°C and similar heating is required to be continued at the time of hardening molding.

[0004]

[Problems the invention solves]

The present invention has been devised to solve the problems mentioned above and it aims at offering a composite that has excellent storage stability, shows satisfactory hardening property by active energy ray irradiation such as ultraviolet rays, has excellent handling property and excellent balance between refractive index and flowability, and optical material having high refractive index and transparency after hardening.

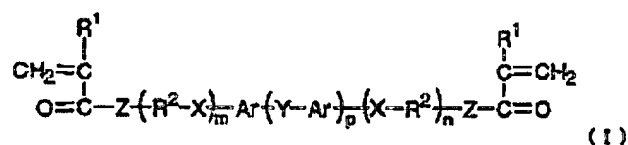
[0005]

[Method to solve the problems]

The authors of the present invention carried out an earnest research in the view of problems mentioned above as a result of which they showed that composite showing satisfactory hardening property and excellent handling property from the viewpoint of balance between refractive index and flowability and optical material having high refractive index and transparency can be offered based on containing a specific quantity of polymerization preventing agent and polymerization initiator in the sulfur-containing (metha) acrylate shown by the general formula (I). Based on this knowledge, the present invention was completed. Namely, the present invention relates to the photo-hardening composite that has characteristic of containing sulfur-containing (metha) acrylate compound shown by the general formula (I) or radical reactive composite containing the same (A), 0.001 ~ 0.5 parts by weight of polymerization preventing agent (B) with respect to 100 parts by weight of component (A) and polymerization initiator (C), and hardened material obtained by hardening the same.

[0006]

[Formula 4]



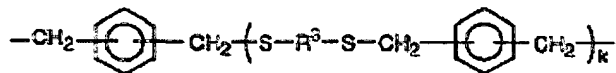
[0007]

[Wherein, R<sup>1</sup> shows hydrogen atom or methyl radical, R<sup>2</sup> shows univalent hydrocarbon radical having 1 ~ 12 carbon atoms, Ar shows arylene radical having 6 ~ 30 carbon atoms that can be substituted with halogen atom excluding fluorine atom or alalkylene having 7 ~

30 carbon atoms that can be substituted with halogen atom excluding fluorine atom, X shows – O – or – S –, when X shows – O –, Y shows – S – or – SO<sub>2</sub> – and when X shows – S –, Y shows – S –, – SO<sub>2</sub> –, – CO –, alkylene radical having 1 ~ 12 carbon atoms, alalkylene radical having 7 ~ 30 carbon atoms, – Ar – (Y – Ar)<sub>p</sub> – shows radical chosen from oligomer shown by

[0008]

[Formula 5]



[0009]

(Wherein, R<sup>3</sup> shows alkylene radical having 1 ~ 12 carbon atoms that can possess ether bond, k shows average oligomerization degree and is 1 ~ 5) or oligomer shown by

[0010]

[Formula 6]



[0011]

(Wherein, l shows average oligomerization degree and is 1 ~ 5), Z shows – O – or – S –, m and n are integers from 1 ~ 5 and p is integer from 0 ~ 10.]

[0012]

[State of practicalization of the invention]

The present research has been explained below in further details. Sulfur-containing (metha) acrylate compound or radical reactive composite containing the same (A) used in the present invention contains sulfur-containing (metha) acrylate shown by the general formula (I). In the present invention, (metha) acrylate means both methacrylate and acrylate. Radical reactive composite containing sulfur-containing (metha) acrylate compound means mixture of compound shown by the general formula (I) with reactive monomer, reactive oligomer or polymer etc. The compound shown by the general formula (I) shows high refractive index and possesses balanced structure due to which it is compatible with different solvents, reactive monomers, reactive oligomers, polymers etc. In the case of radical reactive composite containing reactive monomer, reactive oligomer, polymer etc. besides the compound shown by the general formula (I), content of the compound shown by the general formula (I) in the radical reactive composite should be more than 50 weight %, desirably more than 70 weight % with respect to total radical reactive composite.

[0013]

In the general formula (I), R<sup>1</sup> shows hydrogen atom or methyl radical. R<sup>2</sup> shows divalent hydrocarbon radical having 1 ~ 12 carbon atoms and this radical is formed from carbon

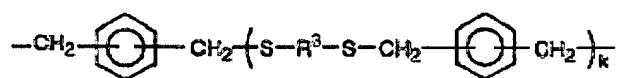
atoms and hydrogen atoms and it should possess 2 bonds. As regards the concrete examples, alkylene radical such as methylene radical, ethylene radical, propylene radical, tri methylene radical, tetra methylene radical, hexa methylene radical, octa methylene radical, deca methylene radical etc. can be given. Alkylene radical having 1 ~ 6 carbon atoms is desired and alkylene radical having 2 ~ 4 carbon atoms is more desired. Ar shows arylene radical having 6 ~ 30 carbon atoms that can be substituted with halogen atom excluding fluorine atom or alalkylene having 7 ~ 30 carbon atoms that can be substituted with halogen atom excluding fluorine atom. As regards the arylene radical having 6 ~ 30 carbon atoms, desirably 6 ~ 12 carbon atoms, phenylene radical, naphthylene radical etc. can be given. As regards the alalkylene radical having 7 ~ 30, desirably 7 ~ 14 carbon atoms,  $-(CH_2)_x - Ar' -$ ,  $- Ar' - (CH_2)_x -$ ,  $-(CH_2)_x - Ar' - (CH_2)_y -$  etc. can be given. Ar' shows arylene radical having 6 ~ 29 carbon atoms such as phenylene radical, naphthylene radical etc., wherein x and y show integers from 1 ~ 24. Sum of carbon atoms of arylene radical shown by x, y and Ar' should be within the range from 7 ~ 30. These arylene radical and alalkylene radical can be substituted with 1 ~ 12 halogen atoms, desirably 2 ~ 8 halogen atoms excluding fluorine atom.

[0014]

X shows  $-O-$  or  $-S-$ . Y shows  $-S-$  or  $-SO_2-$  when X is  $-O-$ , and when X shows  $-S-$ , Y shows  $-S-$ ,  $-SO_2-$ ,  $-CO-$ , alkylene radical having 1 ~ 12 carbon atoms, alalkylene radical having 7 ~ 30 carbon atoms or  $Ar - (Y - Ar)_p -$  shows radical chosen from oligomer shown by

[0015]

[Formula 7]



[0016]

(Wherein,  $R^3$  shows alkylene radical having 1 ~ 12 carbon atoms that can possess ether bond in the chain, k shows average oligomerization degree and is 1 ~ 5) or oligomer shown by

[0017]

[Formula 8]



[0018]

(Wherein, 1 shows average oligomerization degree and is 1 ~ 5). When X is  $-S-$ , Y desirably shows  $-S-$  or  $-SO_2-$ .

[0019]

As regards the concrete examples of alkylene radical having 1 ~ 12 carbon atoms, methylene radical, ethylene radical, propylene radical, tri methylene radical, tetra methylene radical, hexa methylene radical, octa methylene radical, deca methylene radical, do deca methylene radical etc. can be given. Alkylene radical having 1 ~ 6 carbon atoms is desired. As regards the alalkylene radical having 7 ~ 30, desirably 7 ~ 14 carbon atoms,  $-(CH_2)_x - Ar' -$ ,  $-Ar' - (CH_2)_x -$ ,  $(CH_2)_x - Ar' - (CH_2)_y -$  etc. can be given.  $Ar'$  shows arylene radical having 6 ~ 29 carbon atoms such as phenylene radical, naphthylene radical etc. and  $x$  and  $y$  show integers from 1 ~ 24. Sum of carbon atoms of arylene radical shown by  $x$ ,  $y$  and  $Ar'$  should be within the range from 7 ~ 30, desirably 7 ~ 14. Moreover, as regards the alkylene radical having 1 ~ 12 carbon atoms that can possess ether bond in the chain shown by  $R^3$ , radical formed by possessing 1 ~ 5 - O - radicals at any desired position of alkylene radical having 1 ~ 12, desirably 1 ~ 6 carbon atoms can be given.  $Z$  shows - O - or - S -.  $M$  and  $n$  are integers from 1 ~ 5, desirably 1 ~ 3 and  $p$  is an integer from 0 ~ 10, desirably 0 ~ 5.

[0020]

As regards the concrete examples of sulfur-containing (metha) acrylate shown by the general formula (I),  $p$  - bis ( $\beta$  - (metha) acryloyloxy ethyl thio) xylene,  $p$  - bis ( $\beta$  - (metha) acryloyl thio ethyl thio) xylene,  $m$  - bis ( $\beta$  - (metha) acryloyloxy ethyl thio) xylene,  $m$  - bis ( $\beta$  - (metha) acryloyl thio ethyl thio) xylene,  $\alpha$ ,  $\alpha'$  - bis ( $\beta$  - (metha) acryloyloxy ethyl thio) - 2, 3, 5, 6 - tetra chloro -  $p$  - xylene,  $\alpha$ ,  $\alpha'$  - bis ( $\beta$  - (metha) acryloyl thio ethyl thio) - 2, 3, 5, 6 - tetra chloro -  $p$  - xylene, 4, 4' - di ( $\beta$  - (metha) acryloyloxy ethoxy) di phenyl sulfide, 4, 4' - di ( $\beta$  - (metha) acryloyl thio ethoxy) di phenyl sulfide, 4, 4' - di ( $\beta$  - (metha) acryloyloxy ethoxy ethoxy) di phenyl sulfone, 4, 4' - di ( $\beta$  - (metha) acryloyl thio ethoxy ethoxy) di phenyl sulfone, 4, 4' - di ( $\beta$  - (metha) acryloyloxy ethyl thio) di phenyl sulfide, 4, 4' - di ( $\beta$  - (metha) acryloyl thio ethyl thio) di phenyl sulfide, 4, 4' - di ( $\beta$  - (metha) acryloyloxy ethyl thio) di phenyl sulfone, 4, 4' - di ( $\beta$  - (metha) acryloyl thio ethyl thio) di phenyl sulfone, 4, 4' - di ( $\beta$  - (metha) acryloyloxy ethyl thio) di phenyl ketone, 4, 4' - di ( $\beta$  - (metha) acryloyl thio ethyl thio) di phenyl ketone, 2, 4' - di ( $\beta$  - (metha) acryloyloxy ethyl thio) di phenyl ketone, 2, 4' - di ( $\beta$  - (metha) acryloyl thio ethyl thio) di phenyl ketone, 4, 4' - di ( $\beta$  - (metha) acryloyloxy ethyl thio) - 3, 3', 5, 5' - tetra bromo di phenyl ketone, 4, 4' - di ( $\beta$  - (metha) acryloyl thio ethyl thio) - 3, 3', 5, 5' - tetra bromo di phenyl ketone,  $\beta$ ,  $\beta'$  - bis ( $p$  - (metha) acryloyloxy phenyl thio) di ethyl ether,  $\beta$ ,  $\beta'$  - bis ( $p$  - (metha) acryloyl thio phenyl thio) di ethyl ether,  $\beta$ ,  $\beta'$  - bis ( $p$  - (metha) acryloyloxy phenyl thio) di ethyl thio ether,  $\beta$ ,  $\beta'$  - bis ( $p$  - (metha) acryloyl thio phenyl thio) di ethyl thio ether etc. can be given.

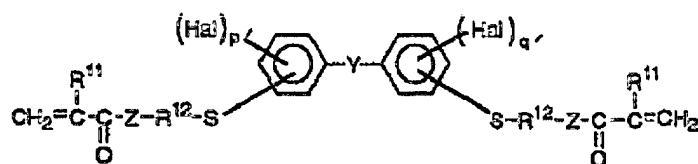
[0021]

Among these compounds shown by the general formula (I), the compound shown by the general formula (II) is desired to be used from the viewpoint of optical properties such as refractive index, color difference.



[0022]

[Formula 9]



[0023]

Wherein,  $R^{11}$  shows hydrogen atom or methyl radical,  $R^{12}$  shows divalent hydrocarbon residual radical having 1 ~ 12 carbon atoms Hal shows chlorine atom or bromine atom, Y shows - S -, -  $SO_2$  - or - CO - and Z shows - O - or - S - and moreover, p' and q' independently show integers from 0 ~ 4. In the general formula (II) mentioned above, the divalent hydrocarbon residual radical having 1 ~ 12 carbon atoms shown by  $R^{12}$  is formed from 1 ~ 12 carbon atoms and hydrogen atoms and it should have 2 bonds. As regards the concrete examples, alkylene radical such as methylene radical, ethylene radical, propylene radical, tri methylene radical, tetra methylene radical, hexa methylene radical, octa methylene radical, deca methylene radical etc. can be given.

[0024]

As regards the concrete examples of sulfur-containing (metha) acrylate compound shown by the general formula (II), 4, 4' - di (β - (metha) acryloyloxy ethyl thio) di phenyl sulfone, 4, 4' - di (β - (metha) acryloyl thio ethyl thio) di phenyl sulfone, 4, 4' - di (β - (metha) acryloyloxy ethyl thio) di phenyl sulfide, 4, 4' - di (β - (metha) acryloyl thio ethyl thio) di phenyl sulfide, 4, 4' - di (β - (metha) acryloyloxy ethyl thio) di phenyl ketone, 4, 4' - di (β - (metha) acryloyl thio ethyl thio) di phenyl ketone, 2, 4' - di (β - (metha) acryloyloxy ethyl thio) di phenyl ketone, 2, 4' - di (β - (metha) acryloyl thio ethyl thio) di phenyl ketone, 4, 4' - di (β - (metha) acryloyloxy ethyl thio) - 3, 3', 5, 5' - tetra bromo di phenyl ketone, 4, 4' - di (β - (metha) acryloyl thio ethyl thio) - 3, 3', 5, 5' - tetra bromo di phenyl ketone etc. can be given.

[0025]

As regards the reactive monomer that can be used by mixing with the compound shown by the general formula (I), mono (metha) acrylate compound such as methyl (metha) acrylate, ethyl (metha) acrylate, n - butyl (metha) acrylate, i - butyl (metha) acrylate, t - butyl (metha) acrylate, 2 - ethyl hexyl (metha) acrylate, lauryl (metha) acrylate, stearyl (metha) acrylate, cyclo hexyl (metha) acrylate, benzyl (metha) acrylate, phenyl (metha) acrylate, phenoxy ethyl (metha) acrylate, phenoxy propyl (metha) acrylate, 2 - hydroxy ethyl (metha) acrylate, 2 - hydroxy propyl (metha) acrylate, 2 - hydroxy butyl (metha) acrylate, 4 - hydroxy butyl (metha) acrylate, glycidyl (metha) acrylate, tetra hydro furfuryl (metha) acrylate, phenyl glycidyl (metha) acrylate, di methyl amino ethyl (metha) acrylate, phenyl cellosolve (metha)

acrylate, di cyclo pentenyl (metha) acrylate, bi phenyl (metha) acrylate, 2 – hydroxy ethyl (metha) acryloyl phosphate etc.; multifunctional (metha) acrylate compound such as ethylene glycol di (metha) acrylate, di ethylene glycol di (metha) acrylate, tri ethylene glycol di (metha) acrylate, tetra ethylene glycol di (metha) acrylate, nona ethylene glycol di (metha) acrylate, 1, 3 – butylene glycol di (metha) acrylate, 1, 4 – butane diol di (metha) acrylate, tri methylol propane tri (metha) acrylate, neo pentyl glycol di (metha) acrylate, 1, 6 – hexa methylene di (metha) acrylate, hydroxy pivalic acid ester neo pentyl glycol di (metha) acrylate, penta erythritol tri (metha) acrylate, penta erythritol tetra (metha) acrylate, di penta erythritol hexa (metha) acrylate, tri (metha) acryloxy ethyl iso cyanulate etc.; mono vinyl compound such as styrene, vinyl toluene, chloro styrene, 1 – vinyl naphthalene, 2 – vinyl naphthalene, N – vinyl – 2 – pyrrolidone etc.; multifunctional vinyl compound such as di vinyl benzene, di vinyl naphthalene etc. can be given.

[0026]

Moreover, as regards the reactive oligomer that can be used by mixing with sulfur-containing (metha) acrylate,

(1) urethane reaction product of hydroxy radical, glycidyl radical or amino radical-containing (metha) acrylate and iso cyanate compound possessing 2 or more iso cyanate radicals in molecule;

(2) epoxy ring opening reaction product of (metha) acrylic acid and epoxy compound possessing at least 1 epoxy radical in molecule;

(3) polyester (metha) acrylate that is reaction product of polyester obtained from multivalent alcohol and polybasic acid and (metha) acrylic acid;

(4) esterification reaction product of (metha) acrylic acid and multifunctional hydroxy compound, esterification reaction product of hydroxyl radical or glycidyl radical-containing (metha) acrylate and multivalent carboxyl compound;

(5) ester exchange (transesterification) reaction product of different (metha) acrylates and multivalent hydroxyl compound etc. can be given.

[0027]

As regards the concrete examples of urethane reaction product of hydroxy radical, glycidyl radical or amino radical-containing (metha) acrylate and iso cyanate compound possessing 2 or more iso cyanate radicals in molecule; 2 – hydroxy ethyl (metha) acrylate, 2 – hydroxy propyl (metha) acrylate, 2 – hydroxy butyl (metha) acrylate, 4 – hydroxy butyl (metha) acrylate; hydroxyl radical-containing (metha) acrylate, addition reaction product of mono epoxy compound and (metha) acrylic acid such as butyl glycidyl ether, 2 – ethyl hexyl glycidyl ether, phenyl glycidyl ether, glycidyl methacrylate etc.; (metha) acrylic acid mono ester such as polyethylene glycol, polypropylene glycol etc. can be given.

[0028]

As regards the concrete examples of iso cyanate compound possessing 2 or more iso cyanate radicals in molecule, aliphatic, aromatic or alicyclic iso cyanate such as tetra methylene di iso cyanate, hexa methylene di iso cyanate, tri methyl hexa methylene di iso cyanate, dimer acid di iso cyanate, cyclo hexane di iso cyanate, iso frone (?) di iso cyanate, tolulyne di iso cyanate, xylilene di iso cyanate, di phenyl methane di iso cyanate, m – phenylene di iso cyanate, di cyclo hexyl methane di iso cyanate, naphthalene di iso cyanate, bi phenyl di iso cyanate etc. can be given and moreover, compound possessing at least 1 iso cyanate radical in the molecule obtained by reaction between these iso cyanates and compound possessing at least 1 active hydrogen atom such as amino radical, hydroxyl radical, carboxyl radical, water etc., or trimer ~ pentamer of the iso cyanate compounds mentioned above can also be used. Urethane formation reaction between hydroxyl radical-containing (metha) acrylate and iso cyanate compound possessing 2 or more iso cyanate radicals in molecule mentioned above can be carried out by well-known method for example, by dropping the mixture of hydroxyl radical-containing (metha) acrylate and catalyst such as di butyl tin di laurate in the presence of iso cyanate compound at 50<sup>0</sup>C ~ 90<sup>0</sup>C.

[0029]

As regards the concrete examples of epoxy ring opening reaction product of (metha) acrylic acid and epoxy compound possessing at least 1 epoxy radical in molecule; epoxy compound possessing at least 1 epoxy radical in molecule, glycidyl ester of aromatic and alicyclic epoxy compound and aliphatic multivalent carboxylic acid such as bis phenol A di glycidyl ether, bis phenol F di glycidyl ether, phenol norvolac glycidyl ether, cresol norvolac glycidyl ether etc., dimer ~ pentamer of these epoxy compounds can be used.

[0030]

As regards the multivalent carboxyl compound, anhydrous di carboxylic acid such as anhydrous phthalic acid etc. Can be used. The reaction of adduct of epoxy compound and (metha) acrylic acid or hydroxyl radical-containing (metha) acrylate and multivalent carboxyl compound such as anhydrous di carboxylic acid for example anhydrous phthalic acid can be carried out by well-known methods such as heating the mixture of epoxy compound and (metha) acrylic acid and catalyst such as tertiary amino compound for example di methyl amino ethyl methacrylate, quaternary amine salt at 60 ~ 110<sup>0</sup>C. As regards the concrete examples of polyester (metha) acrylate that is the reaction product of multivalent alcohol and polybasic acid; polyester acrylate, condensation reaction product of (metha) acrylic acid and polyester obtained from multivalent alcohol such as ethylene glycol, 1, 4 – butane diol, 1, 6 – hexane diol, di ethylene glycol, tri methylol propane, di propylene glycol, polyethylene glycol, polypropylene glycol etc. and polybasic acid such as phthalic acid, adipic acid, maleic acid, trimeric acid, itaconic acid, succinic acid, terephthalic acid etc.

can be given. Reaction between multivalent alcohol and polybasic acid is carried out by heating these at 200<sup>0</sup>C in the presence of catalyst such as di butyl tin oxide etc. to obtain polyester and this is further subjected to condensation reaction with (metha) acrylic acid at 100<sup>0</sup>C to form condensation reaction product.

[0031]

As regards the reactive oligomer, other than those mentioned above, oligo (metha) acrylate obtained by esterification reaction between (metha) acrylic acid and compound obtained by n mole adding ethylene oxide or propylene oxide to bis phenol A, bis phenol F or bis phenol S can be given. As regards the reactive monomer and reactive oligomer used jointly with sulfur-containing (metha) acrylate compound, monomer and oligomer containing halogen atom excluding fluorine, aromatic ring and / or sulfur atom is desired in the case of using the hardened material of photo-hardening resin in the application requiring high refractive index.

[0032]

Other than the monomer and oligomer containing aromatic ring, halogen atom mentioned above, bis (4 – methacryloyl thio phenyl) sulfide, 2, 4, 6 – tri bromo phenyl (metha) acrylate, 2, 4, 6 – tri bromo phenyl ethyl (metha) acrylate, 2, 2 – bis [3, 5 – di bromo – 4 – (2 – methacryloyloxy ethoxy) phenyl] propane etc. can be added within such a range that effect of the present invention is not lost.

[0033]

Polymer used for regulating viscosity, preventing polymerization shrinkage, imparting flexibility can be mixed with the radical reactive composite. As regards the concrete examples, non-reactive polymers such as polyethylene glycol, polypropylene glycol, polyethylene glycol, mono alkyl ether, polypropylene glycol mono alkyl ether, ethylene oxide or propylene oxide adduct of bis phenol A, ethylene oxide or propylene oxide adduct of tetra bromo bis phenol A or different poly (metha) acrylate etc. or polymer possessing reactive radical such as poly (metha) acrylate that possesses reactive radical such as amino radical, hydroxyl radical, epoxy radical, vinyl radical, iso cyanate radical, carboxyl radical, mercapto radical etc. at the terminal or in the side chain can be given. The molecular weight should be within the range from 1000 ~ 5000000 in terms of weight-average molecular weight and it is desired to be within the range from several 1000 ~ 200000 for showing compatibility.

[0034]

As regards the polymerization preventing agent (B) used in the present invention, aromatic amines such as hydroquinone, p – methoxy phenol, 2 – t – butyl hydroquinone, 2, 5 – bis (1, 1, 3, 3 – tetra methyl butyl) hydroquinone, 2, 5 – bis (1, 1 – di methyl butyl) hydroquinone etc.; 2, 2 – di phenyl picryl hydrazyl (DPPH), tri – p – nitro phenyl methanol,

di - p - fluoro phenyl amine, N - (3N - oxy anilino - 1, 3 - di methyl butylidene) - aniline oxide, 2, 2, 6, 6 - tetra methyl piperidine - 1 - oxyl (TEMPO), quaternary ammonium chloride such as benzyl tri methyl ammonium chloride etc.; di ethyl hydroxyl amine, cyclic amide, nitrile compound, substituted urea, benzo thiazol, 4 - amino - 2, 2, 6, 6 - tetra methyl piperidine, bis - (1, 2, 2, 6, 6 - penta methyl - 4 - pipeziny) sebacate, organic acids such as lactic acid, oxalic acid, citric acid, tartaric acid, benzoic acid etc.; t - butyl pyrro catechol, organic phosphine, phosphorous acid salt etc. can be given. The addition quantity of polymerization preventing agent (B) should be within the range from 0.001 ~ 0.5 parts by weight, desirably 0.005 ~ 0.3 parts by weight with respect to 100 parts by weight of component (A). If the quantity of polymerization preventing agent is less, then storage stability reduces whereas if it is more, then hardening becomes insufficient and polymerization initiator has to be added with excess quantity.

[0035]

As regards the polymerization initiator (C) used in the present invention, photo polymerization initiator for example radical polymerization initiator, cation polymerization initiator are used. As regards the examples, bis (acyl phosphine oxide and (bis) acyl phosphinic acid esters such as 2, 6 - di methyl benzoyl di phenyl phosphine oxide, 2, 4, 6 - tri methyl benzoyl di phenyl phosphine oxide, 2, 4, 6 - tri methyl benzoyl di phenyl phosphinic acid methyl ester, 2, 6 - di chloro benzoyl di phenyl phosphine oxide, 2, 6 - di methoxy benzoyl di phenyl phosphine oxide, bis (2, 6 - di methoxy benzoyl) - 2, 4, 4 - tri methyl - pentyl phosphine oxide, bis (2, 4, 6 - tri methyl benzoyl) - phenyl phosphine oxide etc.; acetophenone group compounds such as 1 - phenyl - 2 - hydroxy - 2 - methyl propane - 1 - on, 1 - hydroxy cyclo hexyl phenyl ketone, 4 - di phenoxy di chloro acetophenone, di ethoxy acetophenone, 1 - (4 - iso propyl phenyl) - 2 - hydroxy - 2 - methyl propane - 1 - on etc.; benzophenone group compounds such as benzoyl methyl benzoate, 4 - phenyl benzophenone, hydroxy benzophenone, 3, 3' - di methyl - 4 - methoxy benzophenone, di phenoxy benzophenone etc.; aromatic di azonium salt; aromatic sulfonium salt; aromatic iodonium salt; metallocene compounds etc. can be given.

[0036]

Photo polymerization initiator can be used independently or as a mixture of 2 or more types and the compound having absorption wavelength of more than 400 nm is desired to be used as at least 1 type. This is because light resistance and weather resistance of the sulfur-containing (metha) acrylate compound shown by the general formula (I) is not satisfactory due to which its deterioration is prevented by adding UV absorption agent by irradiating light of shorter wavelength by cutting it at the time of molding and therefore, composite is required to be hardened by light having long wavelength so that the reaction is not obstructed due to additives and molding method. As regards the compound possessing

absorption wavelength of more than 400 nm, (bis) acyl phosphine oxides are desired to be used. As regards the other photo polymerization initiators, benzophenone, acetophenone having absorption on short wavelength side and excellent surface hardening property, (bis) acyl phosphine oxide having excellent internal hardening property are desired to be used.

[0037]

Moreover, photo hardening and thermal hardening can be jointly used for completing the hardening of photo-hardening composite of the present invention smoothly. In the case of jointly using thermal hardening, photo polymerization initiator and thermal polymerization initiator are desired to be jointly used as polymerization initiator (C). As regards the thermal polymerization initiator, benzoyl peroxide, di iso propyl peroxy carbonate, lauroyl oxide, t-butyl peroxy (2-ethyl hexanoate), azo bis iso butylnitrile etc. can be given. However, the initiator having 10 hour half reduction period temperature of more than 90°C is desired as it is required to be stable without carrying out hardening in the case of heating at 45 ~ 60°C at the time of injection molding etc. As regards the concrete examples, 1, 1-bis (t-butyl peroxy) cyclo hexane, 2, 2-bis (4, 4-di-t-butyl peroxy cyclo hexyl) propane, 1, 1-bis (t-butyl peroxy) cyclo do decane, t-hexyl peroxy iso propyl mono carbonate, t-butyl peroxy maleic acid, t-butyl peroxy 3, 5-tri methyl hexanate, t-butyl peroxy laurylate, 2, 5-di methyl-2, 5-di (m-tri oxy peroxy) hexane, t-butyl peroxy iso propyl mono carbonate, t-butyl peroxy 2-ethyl hexyl mono carbonate, t-hexyl peroxy benzoate, 2, 5-di methyl-2, 5-di (benzoyl peroxy) hexane, t-butyl peroxy acetate, 2, 2-bis (t-butyl peroxy) butane, n-butyl-4, 4-bis (t-butyl peroxy) valerate, di-t-butyl peroxy iso phthalate, α, α'-bis (t-butyl peroxy) di iso propyl benzene, di cumyl peroxide, 2, 5-di methyl-2, 5-di (t-butyl peroxy) hexane, t-butyl cumyl peroxide, di-t-butyl peroxide, 2, 5-di methyl-2, 5-di (t-butyl peroxy) hexane-3 etc. can be given.

[0038]

The quantity of addition of polymerization initiator (C) should be within the range from 0.01 ~ 10 parts by weight, desirably 0.02 ~ 5 parts by weight with respect to 100 parts by weight of component (A). If the quantity of initiator is more than that, then not only internal homogeneity but hue of the hardened resin also deteriorates. On the other hand, if it is less than that, then hardening becomes insufficient. The addition quantity of polymerization preventing agent (B) and polymerization initiator (C) was studied as a result of which it was found out that weight ratio of polymerization initiator and polymerization preventing agent (polymerization initiator (C) / polymerization preventing agent (B) with respect to component (A) gives extremely stable effect. Weight ratio of (C) / (B) should be within the range from 0.05 ~ 5000, desirably 0.1 ~ 2000. When both these are added so that this weight ratio is within this range, then the obtained resin shows excellent long-term storage stability at room temperature and satisfactory stability at 45 ~ 60°C at the time of carrying out

injection molding etc. If this ratio is more than that, then polymerization preventing agent is less due to which the effect of long-term storage stability and the effect of suppressing hardening at the time of heating process such as heating injection molding etc. is not obtained. On the other hand, if it is less than that, then quantity of initiator is less than the quantity of polymerization preventing agent due to which hardening becomes insufficient.

[0039]

Compound possessing thiol radical, ultraviolet rays absorption agent, light stabilizing agent, antioxidants, light sensitivity increasing agents, solvent, mold releasing agents, colorants, fillers and other additives can be appropriately blended with the photo polymerizable composite of the present invention as per requirement. Well-known compounds can be used as these additives.

[0040]

As regards the compound possessing thiol radical, ethyl mercaptan, hexyl mercaptan, octyl mercaptan, do decyl mercaptan, stearyl mercaptan, mercapto ethanol, 1, 2 – ethane di thiol, 1, 3 – propane di thiol, 1, 6 – hexane di thiol, 1, 12 – do decane di thiol, mercapto methyl sulfide, 2 - mercapto ethyl sulfide, 3 - mercapto propyl sulfide, 6 - mercapto hexyl sulfide, 1, 2 – bis – 2 – mercapto ethyl thio ethane, 1, 2 – bis – 3 – mercapto propyl thio ethane, 1, 3 – bis – 2 – mercapto ethyl thio propane, 1, 4 – bis – 2 – mercapto ethyl thio butane, 1, 6 – bis – 2 – mercapto ethyl thio hexane, bis – 2 – (2 – mercapto ethyl thio) ethyl sulfide, 2 – mercapto ethyl ether, 3 – mercapto propyl ether, 6 – mercapto hexyl ether, 1, 4 – cyclo hexane di thiol, bis – 2 – mercapto ethoxy methane, 1, 2 – bis – 2 – mercapto ethoxy ethane, bis – 2 – (2 – mercapto ethoxy) ethyl ether, 1, 4 – benzene di thiol, 1, 3 – benzene di thiol, 1, 2 – benzene di thiol, 4 – t – butyl – 1, 2 – benzene di thiol, 1, 2 – bis (mercapto methylene) benzene, 1, 3 – bis (mercapto methylene) benzene, 1, 4 – bis (mercapto methylene) benzene, 1, 2 – bis (mercapto ethylene) benzene, 1, 3 – bis (mercapto ethylene) benzene, 1, 4 – bis (mercapto ethylene) benzene, 1, 2 – bis (mercapto methylene thio) benzene, 1, 3 – bis (mercapto methylene thio) benzene, 1, 4 – bis (mercapto methylene thio) benzene, 1, 2 – bis (2 - mercapto ethylene thio) benzene, 1, 3 – bis (2 - mercapto ethylene thio) benzene, 1, 4 – bis (2 - mercapto ethylene thio) benzene, 1, 2 – bis (2 - mercapto ethylene methylene) benzene, 1, 3 – bis (2 - mercapto ethylene thio methylene) benzene, 1, 4 – bis (2 - mercapto ethylene thio methylene) benzene, 1, 2 – bis (mercapto methylene oxy) benzene, 1, 3 – bis (mercapto methylene oxy) benzene, 1, 4 – bis (mercapto methylene oxy) benzene, 1, 2 – bis (2 - mercapto ethylene oxy) benzene, 1, 3 – bis (2 - mercapto ethylene oxy) benzene, 1, 4 – bis (2 - mercapto ethylene oxy) benzene, 4, 4' – thio di thio phenol, 4, 4' – bi phenyl thiol, 1, 3, 5 – tri mercapto benzene, tri mercapto ethyl iso cyanulate, penta erythritol tetra thio glycolate, penta erythritol tri thio glycolate, penta erythritol di thio glycolate, penta erythritol tetra mercapto propionate, penta erythritol tri mercapto propionate,

penta erythritol di mercapto propionate, tri methylol propane tri thio glycolate, tri methylol propane di thio glycolate, tri methylol propane tri thio propionate, tri methylol propane di thio propionate, mercapto propyl iso cyanulate etc. can be given.

[0041]

These compounds possessing thiol radical have high refractive index as they contain sulfur atom and show different Abbe number due to which these are used for maintaining and regulating refractive index and Abbe number of the composite. Multifunctional thiol is desired to be used as the compound possessing thiol radical. Concretely, penta erythritols group thiol, iso cyanulate group thiol etc. can be given. Multifunctional thiol has the effect of accelerating reaction and imparting flexibility due to its reactivity and soft skeleton. Furthermore, thiol radical has the ability to connect radical chain and radical accelerate due to which it can improve weather resistance and prevent yellow discoloration at the time of hardening. The quantity with which compound possessing thiol radical is added should be within the range from 1 ~ 30 parts by weight, desirably 2 ~ 15 parts by weight with respect to 100 parts by weight of radical reactive composite. If the quantity of compound possessing thiol radical is less than that, then the effect mentioned above cannot be maintained whereas if it is more than that, then hardening becomes insufficient and bleed out can occur.

[0042]

As regards the ultraviolet rays absorption agent, single benzotriazole or copolymer with ethylene type unsaturated compound group ultraviolet rays absorption agent such as 2 - (2' - hydroxy - 5' - methyl phenyl) benzotriazole, 2 - (2' - hydroxy - 5' - t - butyl phenyl) benzotriazole, 2 - (2' - hydroxy - 5' - octyl phenyl) benzotriazole, 2 - (2' - hydroxy - 4' - octoxy phenyl) - 5 - chloro benzotriazole, 2 - (2' - hydroxy - 3', 5' - di - t - butyl phenyl) benzotriazole, 2 - (2' - hydroxy - 3', 5' - di - t - amyl phenyl) benzotriazole, 2 - (2' - hydroxy - 3' - do decyl - 5' - methyl phenyl) benzotriazole, 2 - (2' - hydroxy - 3', 5' - bis (α, α - di methyl benzyl) phenyl) benzotriazole, 2 - (2' - hydroxy - 3' - t - butyl - 5' - methyl phenyl) - 5 - chloro benzotriazole, 2 - (2' - hydroxy - 5' - (metha) acryloxy ethyl phenyl) - 2H - benzotriazole, 2 - (2' - hydroxy - 5' - (metha) acryloxy ethyl phenyl) - 2H - benzotriazole etc.; benzophenone group ultraviolet rays absorption agent such as single benzotriazole or copolymer with ethylene type unsaturated compound for example 2, 4 - di hydroxy benzophenone, 2 - hydroxy - 4 - methoxy benzophenone, 2 - hydroxy - 4 - n - octoxy benzophenone, 2 - hydroxy - 4 - n - do decyloxy benzophenone, 2 - hydroxy - 4 - benzyloxy benzophenone, 2, 2' - di hydroxy - 4 - methoxy benzophenone, 2 - hydroxy - 4 - methoxy - 2' - carboxy benzophenone, 2 - hydroxy - 4 - methoxy - 5 - sulfoxy benzophenone, 2, 2' - di hydroxy - 4, 4' - di methoxy benzophenone, 2, 2', 4, 4' - tetra hydroxy benzophenone, 2, 2' - di hydroxy - 4, 4' - di methoxy - 5 - sodium sulfoxy benzophenone, bis (5 - benzoyl - 4 - hydroxy - 2 - methoxy phenyl) methane, 2 - hydroxy



- 4 - (metha) acryloxy ethoxy benzophenone, 2 - hydroxy - 4 - (metha) acryloxy ethoxy benzophenone etc.; salicylate group ultraviolet rays absorption agent such as phenyl salicylate, 2, 5 - di - t - butyl - 4 - hydroxy benzoic acid n - hexa decyl ester, 4 - t - butyl phenyl salicylate, 4 - t - octyl phenyl salicylate, 2, 4 - di - t - butyl phenyl - 3', 5' - di - t - butyl - 4' - hydroxy benzoate etc.; cyano acrylate group ultraviolet rays absorption agent such as ethyl ( $\beta$ ,  $\beta$  - di phenyl) cyano acrylate, 2 - ethyl hexyl ( $\beta$ ,  $\beta$  - di phenyl) cyano acrylate etc.; oxalic acid derivative group ultraviolet rays absorption agent such as 2 - ethoxy - 2' - ethyl oxalic acid bis anilide, 2 - ethoxy - 5 - t - butyl - 2' - ethyl oxalic acid bis anilide etc.; benzylidene malonic acid ester such as [(4 - methoxy phenyl) - methylene] di methyl propane dioate etc. can be given.

[0043]

As regards the light stabilizing agent, hindado amine (HALS) group light stabilizing agent such as phenyl - 4 - pipedinyll carbonate, 1, 1 - (1, 2 - ethane diyl) bis (3, 3, 5, 5 - tetra methyl piperidine on), bis (2, 2, 6, 6 - tetra - 4 - pipedinyll) sebacate, bis (N - methyl - 2, 2, 6, 6 - tetra methyl - 4 - pipedinyll) sebacate, tetra quis (2, 2, 6, 6 - tetra methyl - 4 - pipedinyll) - 1, 2, 3, 4 - butane tetra carboxylate, tetra quis (1, 2, 2, 6, 6 - penta methyl - 4 - pipedinyll) - 1, 2, 3, 4 - butane tetra carboxylate, 3 - do decyl - 1 - (2, 2, 6, 6 - tetra methyl - 4 - pipedinyll) pyrrolidine - 2, 5 - dion, N - acetyl - 3 - do decyl - 1 - (2, 2, 6, 6 - tetra methyl - 4 - pipedinyll) pyrrolidine - 2, 5 - dion etc. can be given.

[0044]

As regards the antioxidant, phenol group antioxidants such as 2, 6 - di - t - butyl phenol, 2, 4 - di methyl - 6 - t - butyl phenol, 2, 6 - di - t - butyl - 4 - methyl phenol, 2, 6 - di - t - butyl - 4 - ethyl phenol, 2, 4, 6 - tri - t - butyl phenol, 2, 6 - di - t - butyl - 4 - s - butyl phenol, 2 - t - butyl - 4 - methoxy phenol, vitamin E, 2, 6 - di - t - butyl - 4 - hydroxy methyl phenol, n - octa decyl -  $\beta$  - (4' - hydroxy - 3', 5' - di - butyl phenyl) propionate, 2 - t - butyl - 6 - (3' - t - butyl - 5' - methyl - 2' - hydroxy benzyl) - 4 - methyl phenyl acrylate, propyl gallate, octyl gallate, lauryl gallate, 2, 2' - methylene bis (4 - methyl - 6 - t - butyl phenol), 2, 2' - methylene bis (4 - ethyl - 6 - t - butyl phenol), 4, 4' - methylene bis (2, 6 - di - t - butyl phenol), 2, 2' - methylene bis (4 - methyl - 6 - cyclo hexyl phenol), 2, 2' - di hydroxy - 3, 3' - di ( $\alpha$  - methyl cyclo hexyl) 5, 5' - di methyl di phenyl methane, 2, 2' - ethylidene - bis (4, 6 - di - t - butyl phenol), 2, 2' - butylidene - bis (4 - methyl - 6 - t - butyl phenol), 4, 4' - butylidene - bis (3 - methyl - 6 - t - butyl phenol), tri ethylene glycol - N - bis [3 - (3 - t - butyl - 4 - hydroxy - 5 - methyl phenyl) propionate], 1, 6 - hexane diol bis [3 - (3, 5 - di - t - butyl - 4 - hydroxy phenyl) propionate], 4, 4' - thio bis (6 - t - butyl - m - cresol), 4, 4' - thio bis (3 - methyl - 6 - t - butyl phenol), 4, 4' - thio bis (4 - methyl - 6 - t - butyl phenol), bis (3, 5 - di - t - butyl - 4 - hydroxy benzyl) sulfide, tetra quis [methylene - 3 - (3', 5' - di - t - butyl - 4 - hydroxy phenyl) propionate] methane etc.; phosphorus group

antioxidant such as tri phenyl phosphate, di phenyl nonyl phenyl phosphite, tris (2, 4 – di – t – butyl phenyl) phosphite, tris nonyl phenyl phosphite, di phenyl iso octyl phosphite, 2, 2' – methylene bis (4, 6 – di – t – butyl phenyl) octyl phosphite, di phenyl indecyl (?) phosphite, di phenyl mono (tri decyl) phosphite, phenyl di iso decyl phosphite, phenyl di (tri decyl) phosphite, tris (2 – ethyl hexyl) phosphite, tris (indecyl) phosphite, tris (tri decyl) phosphite, di butyl hydrogen phosphite, tri lauryl tri thio phosphite, 4, 4' – butylidene bis (3 – methyl – 6 – t – butyl phenyl) di – tri decyl phosphite, 3, 5 – di – t – butyl – 4 – hydroxy benzyl phosphite di ethyl ester etc.; sulfur group antioxidant such as di lauryl – 3, 3' – thio di propionic acid ester, di tri decyl – 3, 3' – thio di propionic acid ester, di myristyl – 3, 3' – thio di propionic acid ester, di stearyl – 3, 3' – thio di propionic acid ester, lauryl stearyl – 3, 3' – thio di propionic acid ester, penta erythritol tetra ( $\beta$  - lauryl thio propionate) ester, stearyl thio propionamide, di octa decyl di sulfide, 2 – mercapto benzo imidazole, 2 - mercapto – 6 – methyl benzo imidazole, 1, 1' – thio bis (2 – naphthol) etc.; aromatic amine group antioxidant such as alkylated di phenyl amine for example 4, 4' – di octyl di phenyl amine etc., alkylated N, N' – di acryl – p – phenylene di amine, N – phenyl -  $\beta$  - naphthyl amine, N, N' – di – 2 – naphthyl – p – phenylene di amine etc. can be given.

[0045]

As regards the light sensitivity increasing agent, amine derivative such as tri ethanol amine, tri iso propanol amine, 2 – di ethyl amino benzoic acid, di ethyl amino benzoic acid ethyl, di ethyl amino benzoic acid iso acyl, n – butyl amine, di – n – butyl amine etc., urea derivatives such as o – tri thio urea etc.; sulfur compounds such as sodium di ethyl di thio phosphate, s – benzyl iso tulonium (?), p – toluene sulfinat etc.; nitrile compound such as N, N – di methyl – p – amino benzonitrile, N, N – di methyl p – amino benzonitrile etc.; phosphorus compound such as tri – n – butyl phosphine etc.; N – nitroso hydroxy amine derivative, oxazolidine compound, tetra hydro – 1, 3 – oxadine compound, Michler ketone etc. can be given.

[0046]

The photo hardening composite of the present invention can be used by diluting by solvent etc. The sulfur-containing (metha) acrylate shown by the general formula (I) is soluble in solvent such as acetone, methyl ethyl ketone, tetra hydro furan, ethyl acetate, butyl acetate, toluene etc., however, other organic solvent can be used in combination with other additive.

[0047]

In the case of using (metha) acrylate compound synthesized from iso cyanate compound or iso cyanate compound and polythiol, polyol compound etc. as radical reactive composite, metal compounds such as di butyl tin di laurate, aluminium tri iso propoxide etc., Lewis base such as tertiary amine or tertiary phosphine etc. can be added as catalyst of (thio) urethane

forming reaction.

[0048]

The photo-hardening composite of the present invention is desired to be liquid at room temperature  $\sim 60^{\circ}\text{C}$ . The photo-hardening composite of the present invention can be easily copolymerized by irradiating active energy rays in the presence of polymerization initiator (called as photo polymerization, photo hardening). As regards the active energy rays, ultraviolet rays, visible light rays, infrared rays, electron rays etc. can be used and there is no particular restriction over the same as long as it generates radical by acting with polymerization initiator. It is generally selected as per sulfur-containing (metha) acrylate compound, jointly used monomer, photo polymerization initiator, specific wavelength of sensitivity increasing agent. There is no particular restriction over the light source of light irradiation or heat source at the time of carrying out photo hardening. However, hardening can be smoothly carried out by irradiating parallel, scattered light by using ultraviolet rays source such as high pressure or low pressure mercury lamp, metal halide lamp, short arc lamp, chemical lamp, xenon lamp etc. and moreover, visible laser, infrared ray source can also be used with light sensitivity increasing agent. Polymerization hardening can be carried out without using polymerization initiator by using electron rays.

[0049]

In the case of using molding at the time of photo hardening the photo hardening composite, there is no particular restriction over the shape of the mold. Also, there is no particular restriction over the method of obtaining hardened material by using photo hardening composite of the present invention and well known injection polymerization method or film formation method used in air or inert gas can be used. As regards the representative polymerization methods, the method in which composite mentioned above is injected between the mold (quartz glass) kept on elastomer gasket or spacer and active energy rays are irradiated and it is then taken out, can be given. The quantity of irradiation of light is appropriately selected as per composite and type of photo polymerization initiator, however, it should be within the range from  $0.01 \sim 300 \text{ J/cm}^2$ , desirably  $20 \sim 100 \text{ J/cm}^2$ .

[0050]

The hardened material obtained by hardening the photo hardening composite of the present invention can be given treatments such as annealing by heating after carrying out photo hardening for accelerating hardening and reducing strain and optical strain in the internal part of resin. Annealing is also effective in improving weather resistance, however, it is considered to be due to acceleration of hardening. Moreover, hard coat, reflection preventing coat can be coated or dyeing can be carried out on the surface of the obtained hardened material and surface treatment of selective ions, low molecule scattering etc. can be carried out in lens part.

[0051]

[Effect / result of the invention]

A composite that has excellent storage stability, shows satisfactory hardening property by active energy ray irradiation such as ultraviolet rays, has excellent handling property and excellent balance between refractive index and flowability, and the optical material having high refractive index and transparency after hardening can be offered by the present invention.

[0052]

[Practical examples]

The present invention has been explained below in further details with the help of practical examples. However, the present invention is not restricted only to these practical examples. Moreover, refractive index was measured at 25<sup>0</sup>C by Na(d) rays using Abbe refractometer. Change in viscosity was measured at 45<sup>0</sup>C by E type viscometer. In the measurement of hardness, Vacol (?) hardness measuring device Soft Type was used and it was measured on 5 back and 5 front surfaces and average of 10 was taken.

[0053]

<Practical example 1>

0.1 parts by weight of p – methoxy phenol, 0.1 parts by weight of 2, 4, 6 – tri methyl benzoyl di phenyl phosphine oxide (BASF Japan make “Ruciline (?) TPO”) and 0.04 parts by weight of benzophenone were added to 100 parts by weight of 4, 4’ – di (β - methacryloyloxy ethyl thio) di phenyl sulfone and it was stirred and mixed homogeneously at 60<sup>0</sup>C for 1 hour after which de-bubbling (removal of bubbles) was carried out when photo hardening composite was obtained. Next, composite mentioned above heated at 45<sup>0</sup>C was injected in the injection molding containing in which 2 mirror-surface finish quartz glasses having diameter of 80 mm were placed opposite with the space of 2 mm and these were surrounded by gasket made of ethylene – vinyl acetate copolymer, and it was kept undisturbed till it returns to room temperature. After that, irradiation was carried out by metal halide lamp 30 mW/cm<sup>2</sup> with the quantity of 12 J/cm<sup>2</sup> when uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.64 and hardness was 86. On the other hand, the photo hardening composite mentioned above was kept at 25<sup>0</sup>C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45<sup>0</sup>C for approximately 1 month and at 60<sup>0</sup>C for approximately 2 weeks, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0054]

<Practical example 2>

0.2 parts by weight of 1 – hydroxy cyclo hexyl phenyl ketone was used instead of 0.1

parts by weight of 2, 4, 6 – tri methyl benzoyl di phenyl phosphine oxide of practical example 1. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.64. On the other hand, the photo hardening composite mentioned above was kept at 25<sup>0</sup>C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45<sup>0</sup>C for approximately 1 month and at 60<sup>0</sup>C for approximately 2 weeks, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0055]

<Practical example 3>

50 parts by weight of 4, 4' – di (β - methacryloyloxy ethyl thio) di phenyl sulfone and 50 parts by weight of p – bis (β - methacryloyloxy ethyl thio) xylene were used instead of 100 parts by weight of 4, 4' – di (β - methacryloyloxy ethyl thio) di phenyl sulfone of practical example 1 and 0.05 parts by weight of di ethylene hydroxy amine was added. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.62. On the other hand, the photo hardening composite mentioned above was kept at 25<sup>0</sup>C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45<sup>0</sup>C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0056]

<Practical example 4>

50 parts by weight of di ethylene glycol di methacrylate was used instead of 50 parts by weight of p – bis (β - methacryloyloxy ethyl thio) xylene of practical example 3 and quantity of p – methoxy phenol was changed from 0.1 to 0.06 and di ethyl hydroxy amine was not added. Other than this change, procedure similar to practical example 3 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.57. On the other hand, the photo hardening composite mentioned above was kept at 25<sup>0</sup>C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45<sup>0</sup>C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0057]

<Practical example 5>

50 parts by weight of tetra ethylene glycol di methacrylate was used instead of 50 parts by weight of di ethylene glycol di methacrylate of practical example 4. Other than this

change, procedure similar to practical example 4 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.57. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45°C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0058]

<Practical example 6>

95 parts by weight of 4, 4' – di (β - methacryloyloxy ethyl thio) di phenyl sulfone and 5 parts by weight of glycidyl methacrylate were used instead of 100 parts by weight of 4, 4' – di (β - methacryloyloxy ethyl thio) di phenyl sulfone of practical example 1 and quantity of p – methoxy phenol was changed from 0.1 parts by weight to 0.09 parts by weight. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.62. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45°C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0059]

<Practical example 7>

90 parts by weight of 4, 4' – di (β - methacryloyloxy ethyl thio) di phenyl sulfone and 10 parts by weight of 2, 4, 6 – tri bromo phenyl methacrylate (Daiichi Kogyo Seiyaku make, “BR – 30M”) were used instead of 100 parts by weight of 4, 4' – di (β - methacryloyloxy ethyl thio) di phenyl sulfone of practical example 1 and quantity of p – methoxy phenol was changed from 0.1 parts by weight to 0.09 parts by weight. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.64. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45°C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0060]

<Practical example 8>

10 parts by weight of 2, 2 – bis [3, 5 – di bromo – 4 – (2 – methacryloyloxy ethoxy) phenyl] propane (Daiichi Kogyo Seiyaku make, “BR – 30M”) was used instead of 2, 4, 6 – tri

bromo phenyl methacrylate of practical example 7. Other than this change, procedure similar to practical example 7 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.63. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45°C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0061]

<Practical example 9>

Quantity of 2, 4, 6 – tri methyl benzoyl di phenyl phosphine oxide of practical example 1 was changed from 0.1 parts by weight to 0.2 parts by weight and irradiation was carried out by cutting the wavelength of less than 390 nm of the light source. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.64. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45°C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0062]

<Practical example 10>

0.2 parts by weight of 1 – hydroxy cyclo hexyl phenyl ketone (Chiba Specialty chemicals make, “Ingacure 184”) was used instead of 0.04 parts by weight of benzophenone of practical example 1. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.64. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing crystallization even after approximately 3 weeks. Moreover, when it was kept at 45°C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0063]

<Practical example 11>

100 parts by weight of 4, 4’ – di (β - acryloyloxy ethyl thio) di phenyl sulfone was used instead of 100 parts by weight of 4, 4’ – di (β - methacryloyloxy ethyl thio) di phenyl sulfone of practical example 1. Other than this change, procedure similar to practical example 1 was carried out and uniform transparent hardened material was obtained. The refractive index of the obtained hardened material was 1.64. On the other hand, the photo hardening composite mentioned above was kept at 25°C when it remained uniform transparent without undergoing

crystallization even after approximately 3 weeks. Moreover, when it was kept at 45<sup>0</sup>C for approximately 1 month, no change such as increase in viscosity or coloration was observed and it maintained its initial properties.

[0064]

<Practical example 12>

Photo hardening composite of practical example 1 was diluted with 50 parts by weight of toluene and a film was formed on PET film using this dilute liquid by an applicator of 50  $\mu\text{m}$  and it was heated in an hot-air oven of 100<sup>0</sup>C for 2 hours when toluene evaporated. After that, it was put in the glass container made of quartz flown with nitrogen and irradiation was carried out by high pressure mercury lamp 30 mW/cm<sup>2</sup> with the quantity of 24 J/cm<sup>2</sup> under non- oxygen atmosphere when transparent coat layer was obtained.

[0065]

<Comparative example 1>

Quantity of p – methoxy phenol of practical example 1 was changed from 0.1 parts by weight to 0.0005 parts by weight. Other than this change, procedure similar to practical example 1 was carried out and photo hardening composite was obtained. Increase in viscosity was observed in the process of stirring homogeneously at 60<sup>0</sup>C for 1 hour in the manufacture of photo hardening composite and moreover, when the obtained photo hardening composite was kept at 45<sup>0</sup>C, it underwent gelation in few days.

[0066]

<Comparative example 2>

Quantity of p – methoxy phenol of practical example 1 was changed from 0.1 parts by weight to 1 parts by weight. Other than this change, procedure similar to practical example 1 was carried out and hardened was obtained. Refractive index of the obtained hardened material was 1.63 and hardness was 83 which was insufficient.

[0067]

<Comparative example 3>

1 parts by weight of di ethyl hydroxy amine was used instead of 1 parts by weight of p – methoxy phenol of comparative example 2. Other than this change, procedure similar to comparative example 2 was carried out and hardened material was prepared. Hardness of the obtained hardened material was insufficient and the hardened material got deformed when taking it out from the mold and hardness could not be measured as it was very soft.

[0068]

<Comparative example 4>

100 parts by weight of 2, 2 – bis [3, 5 – di bromo – 4 – (2 – methacryloyloxy ethoxy) phenyl] propane (Daiichi Kogyo Seiyaku make, “BR – 42M”) was used instead of 100 parts by weight of 4, 4’ – di ( $\beta$  - methacryloyloxy ethyl thio) di phenyl sulfone of practical example



1 and when stirring was carried out at 80<sup>0</sup>C for 1 hour instead of 60<sup>0</sup>C. Other than this change, procedure similar to practical example 1 was carried out and photo hardening composite was prepared and then hardened material was prepared. However, in the step of putting the photo hardening composite in the injection molding glass container and keeping it till temperature becomes that of room temperature, it became solid.

[0069]

<Comparative example 5>

bis (4 – methacryloyl thio ethoxy) phenyl sulfide (Sumitomo Seika make, “MPSMA”) was used instead of 4, 4’ – di (β - methacryloyloxy ethyl thio) di phenyl sulfone of practical example 1 and when stirring was carried out at 80<sup>0</sup>C for 1 hour instead of 60<sup>0</sup>C. Other than this change, procedure similar to practical example 1 was carried out and photo hardening composite was prepared and then hardened material was prepared. However, in the step of putting the photo hardening composite in the injection molding glass container and keeping it till temperature becomes that of room temperature, it became solid. The evaluation results of composites of practical examples 1 ~ 11 have been given in table – 1 and that of composites of comparative examples 1 ~ 5 have been given in table – 2.

[0070]

[Table 1]

Component		Practical example 1	Practical example 2	Practical example 3	Practical example 4	Practical example 5	Practical example 6	Practical example 7	Practical example 8	Practical example 9	Practical example 10	Practical example 11
(A)	4, 4' – di (β - methacryloyloxy ethyl thio) diphenyl sulfone	100	100	50	50	50	95	90	90	100	100	-
	4, 4' – di (β - acryloyloxy ethyl thio) diphenyl sulfone	-	-	-	-	-	-	-	-	-	-	100
	P – bis (β - methacryloyloxy ethyl thio) xylene	-	-	50	-	-	-	-	-	-	-	-
	Di ethylene glycol dimethacrylate	-	-	-	50	-	-	-	-	-	-	-
	Tetra ethylene glycol dimethacrylate	-	-	-	-	50	-	-	-	-	-	-
	Glycidyl methacrylate	-	-	-	-	-	5	-	-	-	-	-
	2, 4, 6 – tribromophenyl methacrylate	-	-	-	-	-	-	10	-	-	-	-
(B)	2, 2 – bis [3, 5 – dibromo – 4 – (2 – methacryloyloxy ethoxy) phenyl] propane	-	-	-	-	-	-	-	10	-	-	-
	P – methoxy phenol	0.1	0.1	0.1	0.06	0.06	0.09	0.09	0.09	0.1	0.1	0.1
(C)	Diethyl hydroxy amine	-	-	0.05	-	-	-	-	-	-	-	-
	2, 4, 6 – trimethyl benzoyl diphenyl phosphine oxide	0.1	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Benzophenone	0.04	-	0.04	0.04	0.04	0.04	0.04	0.04	0.04	-	0.04
	1 – hydroxycyclohexyl phenyl ketone	-	0.2	-	-	-	-	-	-	-	0.2	-
Eva	Refractive index	1.64	1.64	1.62	1.57	1.57	1.62	1.62	1.63	1.64	1.64	1.64



[0071]

[Table 2]

Comp onent		Comp arative examp le 1	Compa rative exempl e 2	Compa rative exempl e 3	Compa rative exempl e 4	Compa rative exempl e 5
(A)	4, 4' - di ( $\beta$ - methacryloyloxy ethyl thio) di phenyl sulfone	100	100	100	-	-
	2, 2 - bis [3, 5 - di bromo - 4 - (2 - methacryloyloxy ethoxy) phenyl] propane	-	-	-	100	-
	Bis (4 - methacryloyl thio phenyl sulfide)	-	-	-	-	100
(B)	P - methoxy phenol	0.0005	1	-	0.1	0.1
	Di ethyl hydroxy amine	-	-	1	-	-
(C)	2, 4, 6 - tri methyl benzoyl di phenyl phosphine oxide	0.1	0.1	0.1	0.1	0.1
	Benzophenone	0.04	0.04	0.04	0.04	0.04
Evalu ation	Refractive index	-	1.63	-	-	-
	Hardness	-	83	Could not be measur ed	-	-
	Time of keeping at 25°C when crystallization was not observed	-	-	-	-	-
	Time when increase in viscosity and coloration were not observed 45°C	Few days	-	-	During prepara tion	During prepara tion
	60°C	-	-	-	Solidifi ed	Solidifi ed

Continued from front page

(51) Int. Cl.<sup>7</sup>

Discrimination

Number

C 09 D 4/06

5/00

181/02		
181/06		
C 09 D 4/06		
181/02		
181/06		
FI		Theme code (reference)
C 09 D 4/06		
5/00	Z	
181/02		
181/06		
C 09 D 4/06		
181/02		
181/06		
(72) Inventor		Tamura Yutaka Ibaraki ken, Inashiki gun, Ami cho, Chuo, 8 cho me, 3 ban, 1 go. Mitsubishi Kagaku Kabushiki Kaisha Tsukuba Kenkyusho Nai (Internal to Tsukuba Research Center of Mitsubishi Chemicals Co. Ltd.)
(72) Inventor		Hayakawa Seiichiro Ibaraki ken, Inashiki gun, Ami cho, Chuo, 8 cho me, 3 ban, 1 go. Mitsubishi Kagaku Kabushiki Kaisha Tsukuba Kenkyusho Nai (Internal to Tsukuba Research Center of Mitsubishi Chemicals Co. Ltd.)
F Theme (Reference)		
	4J011	NA05 VA13 VA17 NA20 NA23 NA27 VB01 VC02 QA03 QA09 QA13 QA19 QA23 QA24 QA40 QB11 SA06 SA07 SA16 SA22 SA24 SA26 SA77 SA79 SA83 SA84 SA85 SA87 TA01 UA01 VA01 WA02 WA06 WA10 ...